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Impact of cold flow properties of biodiesel on engine performance

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A B S T R A C T

In the view of rapid depletion of fossil fuels and rise in price of crude oil, there is emergent focus and need to search for alternative fuels. As we know that there is huge demand of diesel for transportation sector, captive power generation, agricultural sector and industrial sector, to accommodate those demands biodiesel is being viewed as a substitute for diesel. Biodiesel is an engine fuel that is prepared by chemical reaction of fatty acids and alcohol, which usually means combining vegetable oil with methanol in the presence of a catalyst (usually sodium hydroxide). But before using biodiesel as a substitute for engine fuel, there are two major problems associated, first one is “cold flow property of biodiesel” and second one is termed as “stability of biodiesel”. In this paper our main focus will be on cold flow property of biodiesel and its impact on engine performance. Some of the cold flow properties such as cloud point, pour point and cold filter plugging point are responsible for solidification of fuel causing blockage in fuel lines filters which further leads to fuel starvation in engine operation during starting operation. This paper also provides several remedial measures for improving the cold flow properties of biodiesel.

Contents

1. Introduction

Today the world is facing the crises of exhaustion of fossil fuels due to rapid industrialization, which further leads to environmental degradation. The extraction and consumption of fossil fuels

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in abundance have led to reduction in petroleum reserves. These finite reserves are highly concentrated to certain regions of the world. Therefore, countries which are not having these resources are facing foreign exchange crisis, mainly due to the import of crude petroleum oil. Hence it is necessary to look for other alternative fuels, which can be produced from renewable energy sources like solar, hydro, wind and bio fuel [1]. The vegetable oils are used as alternative fuels from around one hundred years, when the inventor of the diesel engine Rudolph Diesel first tested peanut oil in his compression-ignition engine. In 1970, scientists discovered that the viscosity of vegetable oils could be reduced by a simple chemical process and that it could be used as diesel fuel in modern engine. Considerable efforts have been made to develop a vegetable oil derivative that resembles the properties and performance of the hydrocarbon-based diesel fuels. In Indian perspective the non edible oil can be used as an alternative source of fuel [2]. We know that among non edible plant sources like *neem, mahua, Sal, Jatropha, Pongamia*, major source of biodiesel are *Jatropha* and *Pongamia*, since other plants have medicinal and other uses.

But in the use of non edible oil as fuel there are some major problems associated with them. First one is oxidation stability of biodiesel and other is cold flow properties of biodiesel. It was reported that the combustion characteristics of biodiesel are similar to diesel and the blends were found to be having shorter ignition delay, higher ignition temperature, higher ignition pressure and peak heat release [3].

2. Biodiesel

Biodiesel is defined as the mono alkyl esters of vegetable oils or animal fats. The biggest advantage of biodiesel over gasoline and petroleum diesel is its environmental friendly nature. Biodiesel burns similar to petroleum diesel as it contains regulated pollutants. On the other hand, biodiesel probably has better efficiency than gasoline [2].

Table 1 shows the ASTM and IS standard for diesel and biodiesel. The high kinematic viscosity of biodiesel is the main problem in engine operation because high kinematic viscosity leads to poor combustion and results in carbon deposit and smoke emission [3].

3. Problem of using biodiesel

There are two main problems associated with the use of biodiesel as an alternative of diesel. These are poor cold flow properties and there stability. The various researchers have tried to find out the solution of these problems. Jain and Sharma [5] states that biodiesel consists of long chain fatty acid esters derived from feed stocks such as vegetable oils, animal fats and used frying oil, etc. These products may contain more or less unsaturated fatty acids which are prone to oxidation, accelerated by exposure to air during storage and at high temperature and may yield polymerized compounds. Auto oxidation of biodiesel can cause degradation of fuel quality by affecting the stability parameters. Biodiesel stability includes oxidation, storage and thermal stability. Oxidation instability can led to the formation of oxidation products like aldehydes, alcohols, shorter chain carboxylic acids, insoluble, gum and sediment in the biodiesel.

Thermal instability is concerned with the increased rate of oxidation at higher temperature which in turn, increases the weight of oil and fat due to the formation of insolubles. Storage stability is the ability of liquid fuel to resist change in its physical and chemical characteristics brought about by its interaction with its environment and may be affected by interaction with contaminants, light, factors causing sediment formation, changes in colour and other changes that reduce the clarity of the fuel. These fuel instabilities give rise to formation of undesirable substances in biodiesel and its blends beyond acceptable quantities as per specifications and when such fuel is used in engine, it impairs the engine performance due to fuel filter plugging, injector fouling, deposit formation in engine combustion chamber and various components of the fuel system.

4. Cold flow properties of biodiesel

Crystallization of the saturated fatty acid during winters causes fuel starvation and operability problems as solidified material clogs to fuel lines and filters. With decreasing temperature more solid is formed and material approaches the pour point which is the lowest temperature at which it will cease to flow. It has been well established that the presence of higher amount of saturated components increases the cloud point and pour point of biodiesel utilization of additives that enhance the impact of crystal morphology and blending with a fuel like kerosene which causes freezing point depression [6].

There is no single best way to assess low temperature performance, and the existing fuel standards (both U.S. and European) do not include explicit specifications for cold flow properties for either conventional diesel or biodiesel. However, the fuel provider is generally required to give an indication of the cold flow properties by reporting the cloud point (CP) of the fuel. A number of other laboratory tests are commonly used to define low temperature properties of biodiesel, poor cold flow properties

Table 1
Specification of diesel and biodiesel fuels [4].

Fuel property Fuel standard	Bio diesel IS 15607	Bio diesel ASTM D 6751	Diesel IS 1460	Diesel ASTM D 975
Lower heating value, Btu/gal	116090	118170	19300	129050
Kinematic viscosity, @ 40 °C	8	4.0–6.0	2.5–4.5	1.3–4.1
Specific gravity, kg/L @ 60 °F	0.85	0.88	0.95	0.85
Density, lb/gal @ 15 °C	8.60	7.328	8.20	7.079
Water and sediment (vol%)	0.005	0.05 Max	.05	0.05 Max
Carbon (wt%)	–	77	86.1	87
Hydrogen (wt%)	–	12	7.48	13
Oxygen, by dif. (wt%)	–	11	1.39	0
Sulfur (wt%)	.02	0.01–0.0024	.035	0.05 Max
Boiling point (°C)	–	315–350	250	180–340
Flash point (°C)	120	100–170	66	60–80
Cloud point (°C)	–	−3 to 12	5	−15 to 5
Pour point (°C)	−15	−15 to 10	3	−35 to −15
Cetane number	46	48–65	51	40–55

are due to the presence of long chain, saturated FA esters present in biodiesel. These properties are defined as follows.

4.1. Cloud point (CP)

Cloud point (CP) is the temperature at which wax form a cloudy appearance. It is measured as the temperature at which wax is first formed first, as the fuel is cooled. The presence of solidified wax thickens the oil, and it clogs to fuel filters and injectors in engines. The wax also accumulates on cold surface and forms an emulsion with water. Therefore, cloud point indicates the tendency of the oil to plug filters or small orifices at cold operating temperatures.

4.2. Pour point (PP)

Pour point (PP) is the lowest temperature at which the fuel becomes semi solid and loses its flow characteristics, which makes it no longer pumpable. Hence, in other words we can say that, it is a measure of the fuel gelling point. The pour point is always lower than the cloud point.

4.3. Cold filter plugging point (CFPP)

Cold filter plugging point (CFPP) is the lowest temperature, expressed in 1 °C, at which a given volume of diesel type of fuel still passes through a standardized filtration device in a specified time when cooled under certain conditions [8]. This gives an estimate for the lowest temperature at which fuel will give trouble free flow in certain fuel systems. This is important as in cold temperate countries, a high cold filter plugging point will clog up vehicle engines more easily.

5. Mechanism of cold flow properties

At low temperature engine operation the fuel particles condense and their gelling formation takes place, which results in crystallization of the molecules of a liquid forming a continuous formation of crystals inside the liquid. For crystallization to occur, the molecules of the liquid must generate sufficient thermodynamic force by strong intermolecular force of interaction. This thermodynamic force is generated when the temperature of the liquid is reduced to below its melting point.

Crystallization occurs in two major and interrelated steps known as nucleation and crystal growth. Nucleation is the first stage of crystallization and it occurs when the molecules of the liquid come together to form solid embryos called crystal lattices or crystallites. Crystal growth is subsequent to nucleation. It involves the growth of the crystal lattices formed. Meanwhile, the lattices grow by the nucleation of the layers of new lattices on the existing ones to form large crystals. This growth continues until a continuous network of crystals is formed which results in disruption of fuel flow causing fuel starvation in the engine, ultimately leading to incomplete combustion which is responsible for starting problem in vehicle during cold season.

6. Operation on engine performance

6.1. Steady state operation—It contains three types of engine operation conditions given below

6.1.1. Idling—Under idling the engine operates at no load and nearly closed throttling

Idling requires rich mixture, as the amount of fresh charge brought in during idling is much less than during full throttle operation due to very small opening of throttle. This result in much larger proportion of exhaust gases being mixed with fresh charge. Under idling condition the pressure in the intake manifold is less due to restriction to air flow. When the intake valve is opened the pressure difference between combustion chamber and intake manifold results in initial backward flow of exhaust gases. As a result of this mixture of fuel, air in combustion chamber is diluted. This results in poor combustion and hence it is necessary to provide more fuel particles by richening the mixture to increase the probability of combustion. The general air to fuel ratio under idling condition is 12 to 12.5 and equivalence ratio under idling condition is greater than 1.

6.1.2. Cruising or normal power range

The exhaust gas dilution problem is insignificant in cruising and the primary aim is to make fuel economy more better. Here, 20 to 80% of throttle opening operation is known as cruising. For better fuel economy, slightly lean mixture is supplied because more oxygen would result in complete combustion of fuel. The general air fuel ratio is 16 to 16.5 and equivalence ratio is less than 1.

6.1.3. Maximum power range

During peak power operations engine requires richer mixture so as to provide better power and prevent over heating of exhaust valve. The general air to fuel ratio is 13 to 13.5 and equivalence ratio is greater than 1.

6.2. Transient operation—The transient operations are divided in two phases

6.2.1. Starting

During starting temperatures are very low and when fuel comes in contact with colder walls it undergoes condensation. Even though air fuel ratio is within normal combustion range, the ratio of vaporised fuel to air is less and hence during starting, very rich mixture must be supplied. The air to fuel ratio is around 3 to 5.

6.2.2. Acceleration

The purpose of opening throttle is to provide increase in torque, when throttle is suddenly opened during acceleration the fuel lays behind due to large inertia and hence rich mixture is required during acceleration. This rich mixture acceleration is provided by device known as economiser.

7. Impact of cold flow operation on engine performance

The various researchers have tried to access the problems of engine operation during cold climate which results in fuel starvation, clogging of fuel filters, incomplete combustion and staring problem etc. Kim et al. [7] examines the cold performance of biodiesel blends in a passenger car and a light duty truck at different temperatures, −16 °C and −20 °C. Six different types of biodiesels derived from soybean oil, waste cooking oil, rapeseed oil, cottonseed oil, palm oil and jatropha oil were blended with different volume ratios (B5 (5 vol% biodiesel–95 vol% diesel), B10 and B20). The cold filter plugging point (CFPP) and the cloud point had an effect on the start ability and driveability of both the passenger car and the light duty truck. The start ability and driveability of the passenger car with all biodiesel blends (B5) was generally good at −20 °C.

The cold flow properties of biodiesel are dictated by the length of the hydrocarbon chains and the presence of unsaturated fatty acids in biodiesel. The Table 2 shows the impact of cold flow properties of biodiesel on engine performance.

Table 2
Impact of cold flow properties of biodiesel on engine performance.

S. no	Biodiesel	Property	Effect on engine	Refs.
1.	Biodiesel	Cold flow property	(1) Biodiesel causes plugging and gumming of filters, lines and injector	[1]
2.	Soyabean biodiesel, Rapeseed biodiesel, Cottonseed biodiesel, Palm biodiesel, Jatropha Biodiesel	Cloud point Cold filter plugging point	(1) Starting Problem due to use of biodiesel in cold condition (2) Driving Problem due to use of biodiesel in cold condition	[7]
3.	Canola Biodiesel	Cold soak filterability	(1) Use of Canola oil biodiesel leads to plugging of fuel lines and fuel filter	[9]
4.	Peanut biodiesel	Cloud point Cold filter plugging point Pour point	(1) Peanut biodiesel cause plugging and gumming of filters and wax formation	[12]
5.	Biodiesel	Cloud point	(1) Biodiesel causes fuel starvation and operation problem which cease the fuel flow in engine	[13]
6.	Biodiesel	Pour point	(1) Biodiesel use in cold climate creates pumping problem in engine	[14]
7.	Biodiesel from vegetable and animal origin containg highly saturated methyl esters	Cold filter plugging point	(1) Vegetable and animal oil contains highly unsaturated fatty acids which improve the cold flow working condition of engine	[17]
8.	Waste cooking biodiesel	Cold filter plugging point	(1) Use of waste cooking biodiesel leads to plugging of fuel lines and filters and creates problem in fuel pumping (2) By the use of surfactants Cold Filter Plugging point was reduced	[18]
9.	Tabocoo oil biodiesel	Cold filter plugging point	(1) Use of different cold flow improver are used to avoid fuel plugging	[19]
10.	Biodiesel	Cloud point	(1) Biodiesel causes solidification of fuel lines in cold condition	[22]
11.	Corn oil biodiesel	Cold flow property	(1) Use of Oxystearin leads to improvement in cold flow property by reducing the wax formation	[23]
12.	Biodiesel	Cold filter plugging point	(1) Biodiesel causes plugging of filter and tubes	[27]
13.	Palm Biodiesel, Castor Biodiesel, Diesel	Cloud point Pour point	(1) Crystallizes of fuel particles begins at low temperature for biodiesel (2) Fuel ceases to flow	[30]
14.	Biodiesel	Cloud point Pour point	(1) Fuel no longer Pump able (2) Pour point is always less than cloud point (3) Fuel Line and pump blockage at low temperature which lead to fuel starvation	[31]
15.	Ural Crude oil mixed with diesel	Cloud point Cold filter plugging point	(1) Use of Ural oil with biodiesel improve the cold flow property (2) It reduces the oxidation stability	[32]
16.	Jatropha biodiesel	Cloud point Cold filter plugging point Pour point	(1) Jatropha biodiesel leads to improvement in cold flow property which overcomes the starting problem of engine in cold condition	[33]
17.	Palm oil biodiesel, Tallow oil biodiesel, Rapeseed biodesel	Cloud point Cold filter plugging point Pour point	(1) Palm oil biodiesel and Tallow oil biodiesel gives poor performance while rape seed oil biodiesel give good performance under cold condition	[34]
18.	Palm oil biodiesel, Jatropha oil biodiesel, Castor oil biodiesel	Cloud point Cold filter plugging point Pour point	(1) Thes biodiesel leads to clogging of fuel supply lines and filters and results in poor ignition (2) Cold filter plugging point varies as Castor biodiesel $<$ Jatropha biodiesel $<$ palm biodiesel	[35]
19.	Biodiesel	Pour point	(1) Biodiesel creates fuel starvation in engine due to poor cold flow property (2) Ethanol is good cold flow improver because of its low solidifying temperature of $-114\,^{\circ}C$	[36]
20.	Biodiesel	Cloud point, Cold filter plugging point Pour point	(1) Biodiesel leads to fuel starvation (2) It causes clogging of fuel lines and fuel filters (3) Fuel ceases to flow	[38]
21.	Biodiesel	Cloud point Pour point	(1) Biodiesel leads to crystal formation of fuel (2) Fuel cannot be poured freely	[39]
22.	Biodiesel	Cloud point	(1) Biodiesel leads to fuel clogging	[40]
23.	Vegetable oil	Cold flow property	(1) Use of vegetable oil leads to plugging and gumming of filters, fuel lines and injector	[41]

The above table shows that poor cold properties of biodiesel creates starting and operational problem in engine system which will lead to plugging of fuel lines and filters and engine will not operate. Lin et al. [9] evaluated the impact of saturated monoglycerides, glycerin, and soap on cold soak filterability. Kegl [10] investigated the fuel flow through the whole injection system to all six cylinders with respect to fuel temperature. The pressure drop through the fuel filter and fuelling through each of six injection assemblies were analyzed.

Jain and Sharma [5] studied the thermal stability of biodiesel and their blends with diesel under different conditions. The work revealed that biodiesel is more prone to oxidation when exposed to higher temperature due to the formation of oxidation products like aldehydes, alcohols, shorter chain carboxylic acids, insoluble,

gum and sediment in the biodiesel, which may often be responsible for fuel filter plugging, injector fouling, deposits formation in engine combustion chamber and various components of the fuel system.

Haseeb et al. [11] studied biodiesel, having different chemical characteristics from diesel and suggested that it can interact with materials in a different way. It can cause corrosive and tribological attack on metallic components and degrade elastomer parts. Biodiesel has chemical characteristics that are distinct from that of petroleum diesel. It is therefore expected that it will interact with materials differently.

Perez et al. [12] studied about biodiesel that it has susceptibility to start-up and performance problems consistent with its chemical composition, when vehicles and fuel systems are subjected to cold temperatures. A comprehensive evaluation of the crystallization behaviour of different biodiesels was performed by measuring various defects such as cold filter plugging point (CFPP), cloud point (CP) and pour point (PP). Results were later related to differential scanning calorimetry (DSC) thermograms. Peanut methyl esters in particular led to the most unfavourable properties due to the presence of long-chain saturated compounds. Initially, cooling temperature causes the formation of solid wax crystal nuclei that is submicron in scale and invisible to the human eye, further lowering in temperature causes crystal nuclei to grow. The temperature at which crystals become visible is defined as the cloud point (CP) because the crystals usually form a cloudy or hazy suspension. The temperature at which crystal agglomeration is sufficiently extensive to prevent free pouring of fluid is defined as pour point (PP). The cold filter plugging point (CFPP) is then defined as the lowest temperature at which 40 mL of oil safely passes through the filter within 60 s. The crystallization of these compounds may lead to plugged filters and tubes.

Bhale et al. [13] investigated the performance and emission of ethanol blended Mahua biodiesel fuel and ethanol–diesel blended Mahua biodiesel fuels. A considerable reduction in emission was obtained. Ethanol blended biodiesel is totally renewable, viable alternative fuel for improved cold flow behaviour and better emission characteristics without affecting the engine performance. The cloud point, which usually occurs at a higher temperature than the pour point, is the temperature at which a liquid fatty material becomes cloudy due to the formation of crystals and solidification of saturates. Crystallization of the saturated fatty acids and methyl ester components of biodiesel during cold season causes fuel starvation and operability problems, as solidified material clogs to fuel lines and filters. With decreasing temperature, more solid is formed and material approaches the pour point, at which is flow will cease.

Tang et al. [14] states that the formation of precipitates in biodiesel blends may have serious implications for diesel engine fuel delivery system. Precipitates were observed in Soybean oil (SBO), cottonseed oil (CSO), and poultry fat (PF) based biodiesel blends after storage at 4 °C. As compared to SBO-based biodiesel it is observed that CSO and PF based biodiesel had a lower mass of precipitates. Moreover, different rates of precipitates formation were observed for the B_{20} versus the B_{100} which shows that the formation of precipitate during cold temperature storage was dependent on the feedstock and blend concentration. The solvency effects of biodiesel blends were more pronounced at low temperature than at room temperature leading to a higher amount of precipitates formed.

Sahid and Jamal [16] reviewed the test by using different types of raw and refined oils. When they used raw biodiesel as a fuel, experiments did not show the satisfactory results. The fuel was creating problems such as injector choking and piston ring sticking.

Panoutsou et al. [15] analysed resources available for biodiesel production and identified the most realistic options under technical, economical and environmental perspectives.

Dwivedi et al. [37] states that the torque was decreasing with the increase in biodiesel content due to higher viscosity and lower heating value of biodiesel. The problems in engine that arises due to cold flow property are plugging of fuel filters and fuel lines. Due to nucleation and crystallization there is growth of fuel particles, they further solidify and lead to fuel starvation.

To overcome this engine problem, several remedial measures are suggested by the researchers like use of surfactants and additives or the use of oil such as *Pongamia* for biodiesel production. Since *Pongamia* oil contains highly unsaturated fatty acids, which improve the cold flow property of biodiesel [29].

8. Remedial measures to improve cold flow property of biodiesel

To overcome the problem of cold flow operation, several researchers have provided various methods. Bhale et al. [13] investigated the cold flow properties of 100% biodiesel fuel obtained from Madhuca indica, the cold flow properties of biodiesel were evaluated with and without pour point depressants towards the objectives of identifying the pumping and injecting of these biodiesels in CI engines under cold climate. Effect of ethanol, kerosene and commercial additive on cold flow behaviour of this biodiesel was investigated. A considerable reduction in pour point has been noticed by using these cold flow improvers.

Echim et al. [17] evaluates the effectiveness of different strategies to improve cold flow properties of biodiesel from vegetable and animal origin containing highly saturated methyl esters. The CFPP of the biodiesel samples with poor cold flow properties was improved by formulation with biodiesel samples exhibiting better cold flow properties.

Wang et al. [18] use surfactants and detergent fractionation to improve the cold flow properties of biodiesel from waste cooking oil (BWCO) was investigated. The effect of five types of surfactants, including sugar esters (S270 and S1570), silicone oil (TSA 750S), polyglycerol ester (LOP-120DP) and diesel conditioner (DDA) on the reduction of the cold filter plugging point (CFPP) of the BWCO was evaluated. With the greatest reduction to the CFPP of the BWCO (from -10 °C to -16 °C) was achieved by the addition of 0.02 wt% of polyglycerol ester (LOP-120P). Detergent fractionation of the BWCO was performed by first mixing partially crystallized biodiesel with a chilled detergent (sodium dodecylsulfate) solution accompanied by an electrolyte (magnesium sulphate), and then separating the mixture by centrifugation to obtain the BWCO liquid.

The cold flow properties of biodiesel can be improved by these methods such as, blending it with petroleum diesel and solvents, addition of surfactants, (sugar ester S270, sugar ester S1570, polyglycerol ester LOP-120DP, silicone oil TSA 750, Duralt diesel additive (DDA), Sodium dodecylsulfate (SDS) and magnesium sulphate) and winterization. Usta et al. [19] used Tobacco seed oil as a feedstock for biodiesel production. All properties of the biodiesel that was produced from tobacco seed oil were examined and some solutions were also derived to bring all properties of the biodiesel within European Biodiesel Standard EN14214, to verify biodiesel quality. Among various properties, only oxidation stability and iodine number of the biodiesel, which mainly depends on fatty acid composition of the oil, were not found to be within the limits of the standard. Six different antioxidants which are named as *tert*-butylhydroquinone, butylated hydroxytoluene, propyl gallate, pyrogallol, *a*-tocopherol and butylated hydroxyanisole were used to improve the oxidation stability. Among them, pyrogallol was found to be the most effective antioxidant. The iodine number was improved with the blending of biodiesel produced from tobacco seed oil with a biodiesel that contains more saturated

fatty acids. However, the blending causes increase in the cold filter plugging point. Therefore, four different cold flow improvers, which are ethylene–vinyl acetate copolymer, octadecene-1-maleic anhydride copolymer and two commercial cold flow improvers, are used to decrease cold filter plugging point of the biodiesel and the blends. The best improver is octadecene-1-maleic anhydride copolymer.

Chastek [20] described the Methods for improving the cold flow properties of canola-based biodiesel. Freezing point depression via dilution is evaluated through controlled studies of methyl stearate freezing in seven different solvents, and methyl palmitate in three solvents. There are a limited number of strategies for improving biodiesel cold flow properties.

One method is winterization of biodiesel, which reduces the level of saturated constituents, for example, via cold filtration. Another method that relies on changing the bulk biodiesel chemical composition is to synthesize biodiesel using alcohols other than methanol.

Joshi et al. [21] investigated the Ethyl Levulinate (ethyl 4-oxopentanoate) as a novel, bio-based cold flow improver for use in biodiesel fuels. The cloud (CP), pour (PP), and cold filter plugging points (CFPP) of biodiesel fuels prepared from cottonseed oil and poultry fat were improved upon addition of ethyl levulinate at 2.5, 5.0, 10.0, and 20.0% (volume). Reductions of 4–5 °C in CP, 3–4 °C in PP and 3 °C in CFPP were observed at 20 vol% ethyl levulinate. The approaches for improving the low temperature operability of biodiesel include blending with petro diesel, transesterification with long- or branched-chain alcohols, crystallization fractionation, and treatment with commercial petro diesel cold flow improver (CFI) additives.

Smith et al. [22] states that protruding alkoxy chain increases the viscosity and improved the low-temperature properties of the longer-chain alkoxy biodiesel. Bi et al. [23] improved the cold flow property of biodiesel (fatty acid methyl ester, FAME) made from corn oil by urea complexation. Effects of processing conditions on the yield of low melting- point biodiesel and its fatty acid composition were investigated. The optimal conditions were as follows: 50 °C stirring temperature, 40 min stirring time, 1:1 (w/w) ratio of urea to FAME, 5:1 (v/w) ratio of methanol to FAME, 20 °C crystallization temperature, and 2 h crystallization time. Under these conditions, the maximum yield of non-urea complexes with a melting temperature range from -52 to -45 °C was found to be 53%, and fatty acid profiles of non-urea complexes were composed of, 0.3% palmitic acid, 23.7% oleic acid, 75.1% linoleic acid, and 0.9% linolenic acid.

Seames et al. [24] evaluated the use of thermal cracking to overcome cold flow and stability limitations of current biodiesel. Experiments were conducted in a batch cracking reactor system using soy methyl ester and canola methyl ester feed stocks. The amount of high-MW C16–C24 FAMEs was reduced from nearly 100% in the original feedstock by an order to 70 to 85%, while cloud and pour points decreased around 20 °C and 15 °C, respectively. The stability of the fuel was improved by converting all of the unsaturated esters into lower-MW saturated esters. This method may lead to an attractive process to produce an improved biodiesel that is more conductive to cold temperature utilization and more stable during storage.

Boshui et al. [25] evaluated the impact of three cold flow improvers namely, olefin-ester copolymers (OECP). Ethylene vinyl acetate co polymer (EACP) and polymethyl acrylate (PMA), on the low temperature properties, and viscosity-temperature characteristics of a soya bean biodiesel was evaluated on a low temperature flow tester and rotary rheometer. The crystal morphologies of biodiesel at low temperature were investigated through a polarizing microscope. The result indicated that the ability of cold flow improvers differed in improving the cold flow properties of soya bean biodiesel but among most of them, OECP was found to be the best candidate. OECP can reduce PP and CFPP of biodiesel and retard viscosity increase of biodiesel at low temperature when incorporated into biodiesel at the additive contents of 0.03%. On the other hand, OECP functions to inhibit the wax crystal from growing to larger size and provides a barrier to crystal agglomeration at low temperature, thus improving the cold flow properties of soya bean biodiesel.

Smith et al. [26] studied about the property of biodiesel that currently limits its use to blends of 20% or less and its relatively poor low-temperature properties. Alkoxylation of the unsaturated portion of biodiesel offers the potential benefit of reduced cloud point without compromising ignition quality or oxidation stability. Conventional biodiesel was synthesised from canola oil and the alcohols such as methanol, ethanol and butanol and, epoxidised in situ, and alkoxylated by acid-catalysed oxirane ring opening in the presence of the alcohol of the ester group. Optimal conditions for epoxidation were, H_2O_2/biodiesel molar ratio of 2:1, acetic acid/biodiesel molar ratio of 0.2:1, 2 wt% H_2SO_4 and 6 h reaction at 60 °C.

Alkoxylation resulted in alkoxy substitution rates of 37.1% (methyl), 34.3% (ethyl) and 32.9% (butyl). Selectivity for alkoxy biodiesel was 89.0%, 82.7% and 81.7% for methoxy, ethoxy and butoxy biodiesel, respectively. The cloud point for methyl and ethyl biodiesel increased slightly, while a reduction of 1 K was achieved for butyl biodiesel. The presence of by-products negated much of the expected improvement in cloud point for butoxy butyl biodiesel. Further optimisation work is required to improve both conversion and selectivity, if significant improvements in cloud point are to be achieved.

Kerschbaum et al. [27] developed the new method for winterization of biodiesel, based on waste cooking oil is demonstrated using micro heat exchangers with channel diameters of 200 μm. Biodiesel is pumped from a vessel through a micro heat exchanger in such a way, that pure seed crystals of saturated fatty acid methyl esters are produced at the outlet of the micro channels and injected back into the biodiesel vessel. Thus micro process engineering allows the reduction of the sum of saturated fatty acid methyl esters within biodiesel from 21.3% to 9.6%, which are based on waste cooking oil.

This corresponds to a reduction in CFPP value of 11 K, which means that this biodiesel can be used at temperatures down to 264 K. In winter crystallization of high melting saturated fatty acid methyl esters may lead to plugging of filters and tubes. A fuel suited for low ambient temperatures must have a low cold filter plugging point (CFPP). There is a correlation between saturated fatty acid methyl esters that is, higher the concentration of saturated compounds, the higher will be CFPP value.

Leung and Guo [28] studied the characteristics and performance of three commonly used catalysts used for alkaline-catalyzed transesterification i.e. sodium hydroxide, potassium hydroxide and sodium methoxide, they were evaluated using edible Canola oil and used frying oil. The fuel properties of biodiesel produced from these catalysts, such as ester content, kinematic viscosity and acid value were measured and compared. With the properties such as, intermediate catalytic activity and a much lower cost, sodium hydroxide was found to be more superior as compared to the other two catalysts.

The above literature survey show that there are various remedial measure to improve the Cloud point, Pour point and Cold filter plugging point which will ultimately lead to improvement in the cold flow behaviour of biodiesel and this will enhance the suitability of biodiesel as fuel in cold climatic conditions.

9. Conclusion

The study shows that there are several problems associated with biodiesel, while we are using it as fuel in engine. Out of various such

problems, the cold flow property of biodiesel is the major one, since it creates the starting problem in engine. In this literature review the various researchers established that the poor cold flow property of biodiesel is the main cause for the plugging of fuel lines and filters, it also creates the fuel starvation in engine, which ultimately leads to ignition problem. Due to ignition problem there will be an incomplete combustion of fuel, which will further lead to starting problem in the engine. To eradicate these problems, various researchers have suggested several remedial measures to improve the cold flow property of biodiesel by blending it with petroleum diesel and solvents, the addition of surfactants and winterization. Cold flow improver like Olefin-ester copolymer and Octa-1-maleic anhydride copolymer also improve the cold flow property of the biodiesel.

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